

## Photocatalysis: semiconductor physics

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## Where do I come from?











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## Guimarães





#### Introduction>>

- **Photocatalysis** is an active, attractive, and growing area regarding the removal of organic pollutants from water and air.
- It is based on the **photonic activation** of a metal oxide (semiconductor) catalyst.
- In order to increase the photocatalytic efficiency of these photocatalysts, it is important to enhance their specific surface area, crystallinity and the absorption of light from the solar spectra amongst other properties.



#### Solar spectrum>>



http://www.marusyosangyo.jp/



#### Photocatalysis mechanism>>

#### Titanium dioxide is

a light-activated catalyst used in the dissociation (cleaning) of organic and inorganic materials.

Bahnemann, D., *Photocatalytic water treatment: solar energy applications*, Solar Energy, 2004, **77**, 445–459

http://photochemistryportal.net/



Process	Name
$TiO_2 + hv \rightarrow h_{VB}^+ + e_{CB}^-$	Charge Separation
$h_{VB}^{+} + H_2O \rightarrow OH^{\bullet}$	OH <sup>•</sup> Generation (VB)
$e_{CB}^{-} + O_2 \rightarrow O_2^{\bullet-} + H_2O \rightarrow OH^{\bullet}$	OH <sup>•</sup> Generation (CB)



Promotion of an **electron** to the conduction band, on irradiation by UV light, results in a 'hole' in the valence band – essentially a detriment of the electron density that was localized on that orbital, and usually assigned a positive charge to symbolize the loss of negative. **The hole** is powerfully oxidizing - the orbital very much wants to retrieve electron density just lost after light irradiation. It can retrieve this simply by the electron in the conduction band recombining with the valence band – **recombination** is a sum of radiative (*i.e.* emission may be observed) and non-radiative processes. Based on the energy gap law, the fact that rutile energy levels are closer mean that the non-radiative process is more efficient, and hence recombination is more efficient.

Alternative pathways to recombination are possible, and as you can guess, these result in the use of these **materials as photocatalysts**. The hole has the potential to oxidize water that may be on the surface of the material resulting in the formation of **hydoxyl radicals**. Hydroxyl radicals are themselves very **powerful oxidisers**, and can easily oxidize any organic species that happens to be nearby, ultimately to carbon dioxide and water. Meanwhile, upstairs in the conduction band, the electron has no hole to recombine with, since the hole has oxidized surface bound water. It quickly looks for an alternative to reduce, and rapidly reduces oxygen to form the superoxide anion. This can subsequently react with water to form, again, the hydroxyl radical.



#### Titanium Dioxide>>

#### TiO<sub>2</sub> holds several advantages:

- High chemical stability
- Excellent functionalization
- Non-toxic
- Cheap to synthesize



# However... in most cases, has the disadvantage of requiring **UV light** to enhance photocatalysis



#### SC band-gap>>



Michael Grätzel, Nature 414, 338-344 (2001)



#### Band-gap tuning>> anionic doping



400 500 600 700 Wavelength (in nanometers)

#### Titania Density of States (DOS)>>



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Asahi, et al., Science Vol. 293, 2001



### **TiO<sub>2</sub> Band Structure**



13 R. Sanjines, et al., Journal of Applied Physics 75 (1994) 2945

Schiffer

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#### band-gap tuning>> cationic doping

By incorporating a small amount of **silver** (1-5%) results in increased efficiency in photocatalysis.

Silver has a "Fermi level" or electron accepting region at an energy just below the  $TiO_2$  conduction band.

Therefore, after light absorption and charge separation, **the electron in the conduction band can be effectively trapped by the silver**, while the hole oxidizes water and forms hydroxyl radicals, **without the threat of recombination**.





### >>TiO<sub>2</sub> Photocatalytic Nanoparticles synthesis







### >>Band-gap measurement

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#### >>Photocatalytic degradation analysis

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#### Nanoparticles immersed in a Methylene Blue solution

#### • UV light (LED 365 nm)





Greater photocatalytic activity under UV radiation in the N-doped samples

#### UV-Vis reactor for photocatalysis experiments>>



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### >>Photocatalytic degradation analysis



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#### Nanoparticles immersed in a Methylene Blue solution

Xenon lamp (400-900 nm)





Mass of doping material significantly influences the photocatalytic behavior of the TiO<sub>2</sub> nanoparticles under visible light 20

#### >>Quantification of \*OH radicals







### Crystallinity assessment (TiO<sub>2</sub> NPs)>>



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#### BET Analysis>>

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## Introduction

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**Magnetron sputtering** is very versatile tool for the **physical vapour deposition (PVD)** of **thin films** for optical, semiconductor, wear and corrosion prevention, photovoltaic, self-cleaning, biomedical applications, to name a few.

These coatings are performed in **high vacuum** and exhibit properties unlike the same bulk materials.







#### Sputtering chamber>>







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#### HI-ERDA: level of N-doping>>



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Depth  $/\times 10^{15}$  at./cm<sup>2</sup>



binding energy difference (O1s-Ti2p<sub>3/2</sub>)= 529.9-457.4=72.5 eV >71.4 eV !!



#### Enhancement in UV-visible catalysis after thermal annealment on glass substrates>>



# Thank you for your attention





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